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INVESTIGATION OF LIGHT SCATTERING IN
HIGHLY REFLECTING PIGMENTED COATINGS

National Aeronautics and Space Administration
Office of Advanced Research and Technology
Washington 25, D.C.

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Report No. IITRI-C6018-13
(Quarterly Report)

INVESTIGATION OF LIGHT SCATTERING IN
HIGHLY REFLECTING PIGMENTED COATINGS

November 1, 1964 to February 1, 1965

Contract No. NASr-65(07)
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FORWARD

This is Report No. IITRI-C6018-13 (Quarterly Report) of
Project C6018, Contract No. NASr-65(07), entitled "Investiga-
tion of Light Scattering in Highly Reflecting Pigmented Coatings."
This report covers the period from November 1, 1964 to February
1, 1965. Previous Quarterly Reports were issued on October
11, 1965 (IITRI-C6018-3), January 29, 1964 (IITRI-C6018-6),
May 5, 1964 (IITRI-C6018-8), September 5, 1964 (IITRI-C6018-11)
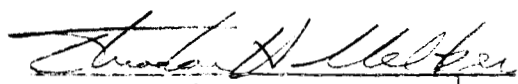and December 21, 1964 (IITRI-C6018-12).

Major contributors to the program include Gene A. Zerlaut
(Project Leader), Dr. S. Katz and Dr. B. Kaye (theoretical
analyses), and V. Raziunas (experimental investigator). Due
to vacations and to the illness of one of us, Mr. V. Raziunas,
only two weeks of experimental work was completed during this
report period. The experimental work performed will be in-
cluded in the next Quarterly Report and will, therefore, not
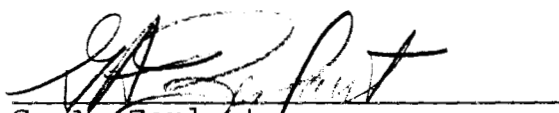be reported at this time.

Data are recorded in Logbooks C14085 and C13906.

Respectfully submitted,

IIT RESEARCH INSTITUTE

Approved by:

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ABSTRACT   17533

    The work discussed in this report represents portions of
two theoretical studies which are being performed in concert.
The approaches consist of the adaptation of both classical light-
scattering theory and a random walk technique to the problem of
multiple interaction. It is planned to assimilate both studies
into an encompasing theoretical analysis of muliple-scattering
phenomena. For example, using classical theory, it is shown
that a film containing $\sim 7 \times 10^8$ particles/cm^2 of 1-μ diameter
and infinite refractive index (totally reflecting) will back-
scatter all radiation below 12.5 μ and will be highly transparent
to wavelengths of 21 μ or longer.

    A required step in the random-walk techniques is the cal-
culation of the average interparticle distance in monosized par-
ticle clouds. It is shown that the average interparticle dis-
tance in symmetrical arrays is a function of the volume concen-
tration only. Also calcualted was the solid angles subtended in
multiple particle systems. Finally, the probability distribution
of interparticle distances within a dilute cloud of particles is
determined and applied to a rain cloud as an example of a real
dilute system.

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INVESTIGATION OF LIGHT SCATTERING IN
HIGHLY REFLECTING PIGMENTED COATINGS

I. INTRODUCTION

As has been noted previously, the principal objective of
this program is the application of light-scattering theory to
particle arrays in an attempt to explain the scattering behavior
of polydisperse pigmented coatings, especially highly reflecting
pigmented coatings. In this respect, the program is aimed at
a definition of the light-scattering parameters associated
with the maximum reflection of solar radiation.

Work thus far has involved (1) a review of the applicable
light-scattering theory with special emphasis on that portion
holding the most promise for application to multiple scattering
phenomena, (2) the conception of theoretical approaches and
techniques with which to treat the problem of multiple scat-
tering, and (3) the generation of experimental data concern-
ing the optical properties of carefully prepared arrays of
silver halide particles dispersed in a matrix.

The studies discussed in the following sections are con-
cerned with the two theoretical approaches outlined above. In
this respect they represent continuing efforts on (1) the
adaptation of classical light-scattering theory to the multiple
interaction problem, and (2) the adaptation of "random walk"
techniques to elucidation of multiple scattering. The two
approaches are preceeding in concert and, as work progresses,

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efforts will be made to assimilate them into an encompasing theoretical analysis of multiple scattering phenomena.

II. APPLICATION OF CLASSICAL THEORY TO MULTIPLE SCATTERING

A. General Consideration

In previous reports we have examined the electromagnetic theory of light scattering when applied to single particles. We have also attempted to consider the application of the theory to multiple arrays of particles. In the present discussion, we shall consider the formation of a theoretical film consisting of a transparent matrix in which the light scattering particles are embedded. Since the system is theoretical it is possible to visualize such convenient factors as fully monodisperse particle assemblies, complete freedom of choice of refractive index, etc. The analysis is handicapped by the limited availability of numerical data. Total and radical scattering data are available for transparent speherical particles over a wide range of conditions. On the other hand, the information for fully reflecting particles with infinite refractive index is fragmentary and only a few cases involving complex refractive indices have been computed. Practically no data exist for non-spherical particles although a number of these appear to have some value in the present context.

In formulating this model, one should note that the Mie theory of light scattering was developed for the case of a parallel light beam impinging on an isolated particle. It

has often been stated that the argument is applicable to particle clouds where the separation distance is "large" and it has also been noted that the viewing optics must be located at "infinity". The second condition is realized adequately when the viewing distance is a few tens of wavelength equivalents separated from the scatterer. The first, the separation distance, is a problem of some magnitude in the present context where we are attempting to replace a diffuse cloud with a close-packed array. This reservation emphasizes the necessity of careful scrutiny of the following operations, especially those involving the application of Mie theory to closely spaced arrays.

Some general relations of use here are noted:

Extinction per Single Particle: If I_o is the intensity of the incident light, in watts per unit area, then a sphere will intercept $K\pi r^2 I_o$ watts from the incident beam, where K, as before, is the scattering or scattering plus absorbing cross-section of the particle and r is the radius of the particle. As noted previously, K is a function of the refractive index of the particle and of the wavelength of the light.

Scattering per Single Particle: The scattered intensity at a distance R from the particle in direction θ is equal to

$$I = \frac{I_o \lambda^2 (i_1 + i_2)}{8 \pi^2 R^2}$$

where i_1 and i_2 are the polarized radial components of the scattered light as usually tabulated.

In a medium containing n particles per unit volume, the scatter per unit volume is nI.

The attenuation of the incident beam as it passes through a particulate array containing n particles per unit volume is given by

$$I = I_o e^{-K\pi r^2 nl} \qquad (2)$$

where l is the length of the path through the particle cloud.

B. Theoretical Films

The first system will consist of a suspension of spherical particles of refractive index, m = ∞, i.e., perfectly reflecting surfaces. It should be recalled (Report No. IITRI-C6018-11) that particles for which the ratio r/λ is very small have a very low effective cross-section. At the other extreme, large particles show the usual preponderance of forward scattering over back scatter. Blumer[1] has computed the total and radial scatter for a number of cases. We shall examine the extinction conditions for the case were α is 0.5.

$\alpha = 0.5$: The ratio of the back scattered intensity of a single particle to the forward scatter is 9:1. Thus extinction of the incident beam in the forward direction is only slightly compensated by forward scatter: and we shall omit consideration of forward scatter.

The values for α and K for totally reflecting spheres as cited by Blumer, are shown in Table 1.

---

[1] Blumer, Z. Physik 38 304 (1962).

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Table 1

LIGHT SCATTERING PARAMETERS FOR TOTALLY REFLECTING SYSTEMS

α	K
0.4	0.086
0.5	0.22
0.6	0.47
0.8	1.26
1.0	2.04
1.2	2.28

Equation 2 will be used for the case of an array of $1\text{-}\mu$ radius spheres. Since $\alpha = 2\pi r/\lambda$, then when $\alpha = 0.5$, $\lambda = 12.5\mu$.

Restating Equation 2,

$$2.303 \log I_o/I = K\pi r^2 N \qquad (2a)$$

where $N = nl$. Replacing K and r with their indicated values, and assigning I_o/I a value of 100, we can compute the number of particles, N, per unit area required to attenuate the beam to 1%;

$$2.303 \log 100 = 0.218\pi (10^{-4})^2 \; N.$$

Solving for N we obtain

$$N = 6.7 \times 10^8 \text{ particles per cm}^2.$$

In a volume of 1 ml, this would correspond to an uniform lattice of particles with center-to-center distances of 10μ. If we use a particle spacing of 4μ in the direction 1, i.e., 2 diameters as suggested by Berry[2] as the limit for the application of scattering theory to closely spaced systems, the films would be 4-mm thick.

[2]Berry, J.O.S.A. _52_ 888 (1962).

We may carry the calculation a stage further by determining the attenuation of light of other wavelengths by this film. Substituting the values for K corresponding to various wavelengths while keeping r equal to 1 μ, it is possible to determine I/I_o. Some representative values are shown in Table 2.

Table 2

ATTENUATION OF LIGHT BY A FILM OF 6.7×10^8 PARTICLES
PER CM^2 OF 1-MICRON RADIUS AND INFINITE REFRACTIVE INDEX

α	(μ)	K	I/I_o
0.3	21.0	0.028	0.48
0.4	15.6	0.086	0.16
0.5	12.5	0.22	0.01
0.6	10.4	0.47	1.6×10^{-5}
0.8	7.8	1.26	2×10^{-16}

Thus it is seen that a film containing 6.7×10^8 particles per spuare centimeter of 1-μ diameter and infinite refractive index will back-scatter all radiation below 12.5 μ and will be highly transparent to wavelengths at 21 μ and longer.

A number of other systems have been computed, using as the reference point the particle concentrations for $\alpha = 0.3$, 0.8 and 1.0 at which the transmission is 1%. The results are shown in Figure 1. Thus, for example, for the case where $\alpha = 1$, a film of 7.2×10^7 particles per cm^2 of 1-μ radius will back-scatter 99% of the 6.28 μ wavelength radiation. All shorter wavelengths will be back-scattered and the film will be transparent to longer wavelengths.

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Figure 1

TRANSMISSION FOR 1 $-\mu$
RADIUS SPHERES, M = ∞

N = particles/cm^3
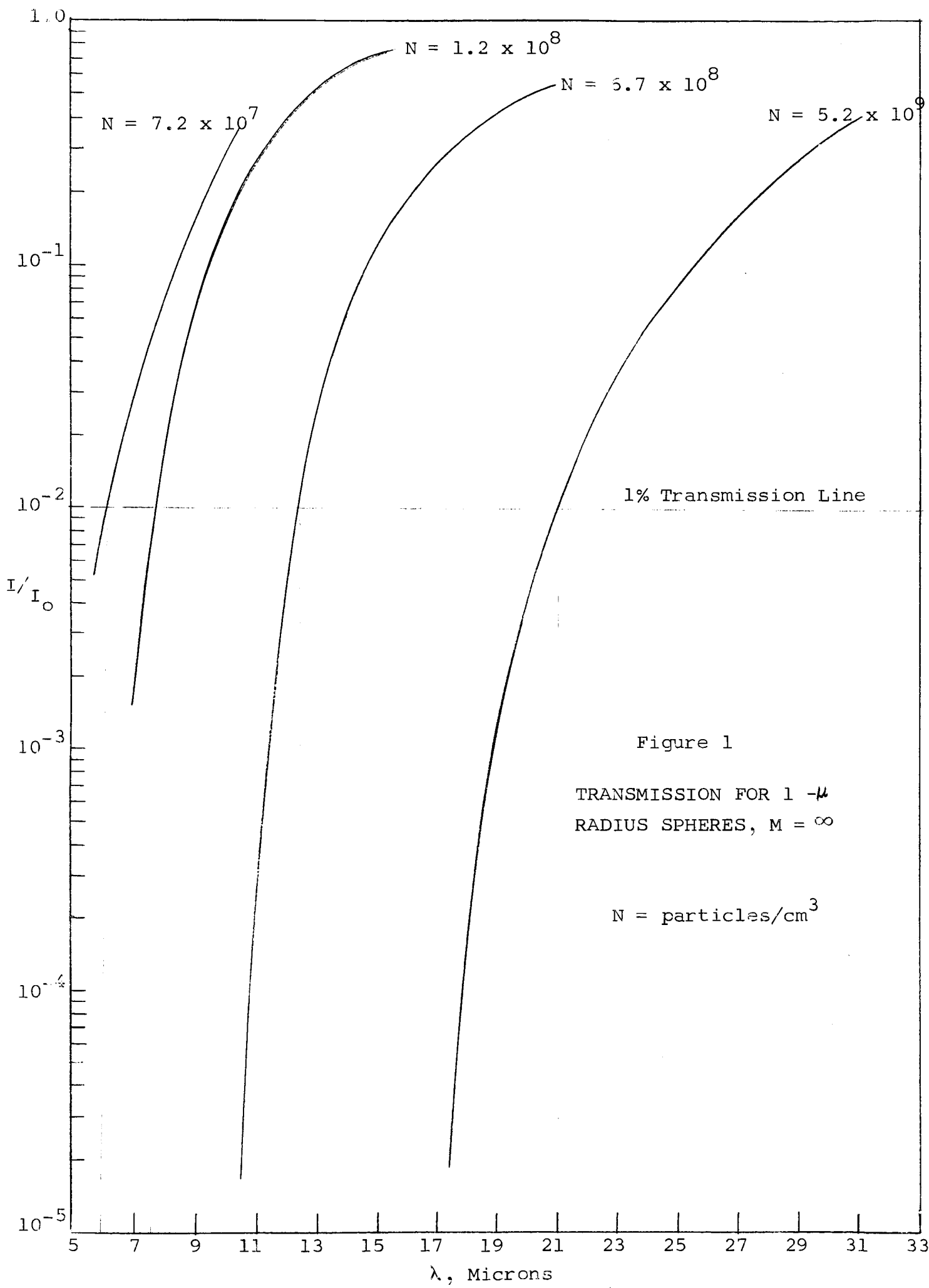
Other systems will be discussed subsequent reports.

III. RANDOM-WALK TECHNIQUE FOR STUDYING MULTIPLE SCATTERING

The ensuing analyses represent the initial steps in the application of "random-walk" techniques to the problem of multiple scattering in highly pigmented systems as discussed in the last Quarterly Report (IITRI-C6018-12). The usefulness and the significance of the relationship developed will become apparent in subsequent reports.

DEFINITION OF TERMS

ε = Volume fraction of empty space in the particle cloud

= Volume fraction of vehicle in collapsed cloud i.e. paint film

n = Number of particles in unit volume of system

Vp = Volume of particle

α = 1-E is volume fraction of particles in a cloud

(note $\dfrac{\alpha}{Vp} = n$)

$\emptyset$ = is the solid angle that the second particle subtends with respect to the center of the prime scattering particle.

σ = Extension factor which is used to take into account that a particle exerts an influence over a greater area than its physical projected area

$F(\Phi)_{xyx}$ = Function defining the energy entering a solid angle Φ which has as its axis the line joining the centroid of the area defining the solid angle, Φ the coordinates of the centroid being x, y, z

V_s = Volume of cloud studied

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A. Average Interparticle Distance within a Monosized Particle Cloud

The simplest average interparticle distance which can be calculated for a monosized system of spheres is that for a system in which the particles are assembled in a symmetrical, cubic array. Such a system is shown in Figure 2. Let x = distance between centers. Now it follows from the symmetry of Figure 2 that each particle occupies a volume x^3 of the array.

$$\therefore \quad \frac{1}{n} = x^3$$

where n = number of particles in unit volume of the system. Now

$$V_p = \frac{1}{6} \pi d^3 \qquad \text{where} \qquad d = \text{diameter of particle}$$
$$V_p = \text{Volume of particle}$$

Therefore

$$n = \frac{\alpha}{V_p} = \frac{\alpha}{\frac{1}{6}\pi d^3} = \frac{6\alpha}{\pi d^3}$$

where α = volume fraction of particles in the cloud.

$$\therefore \quad x^3 = \frac{\pi d^3}{6\alpha}, \quad \text{and} \quad x = d \sqrt[3]{\frac{\pi}{6\alpha}}$$

Let y = number of particle diameters between particle centers.

$$y = \frac{x}{d} = \sqrt[3]{\frac{\pi}{6\alpha}} = 0.806 \times \sqrt[3]{\frac{1}{\alpha}} \qquad (3)$$

From this relation we see that the average interparticle distance in a symmetrical array is a function of the volume concentration only.
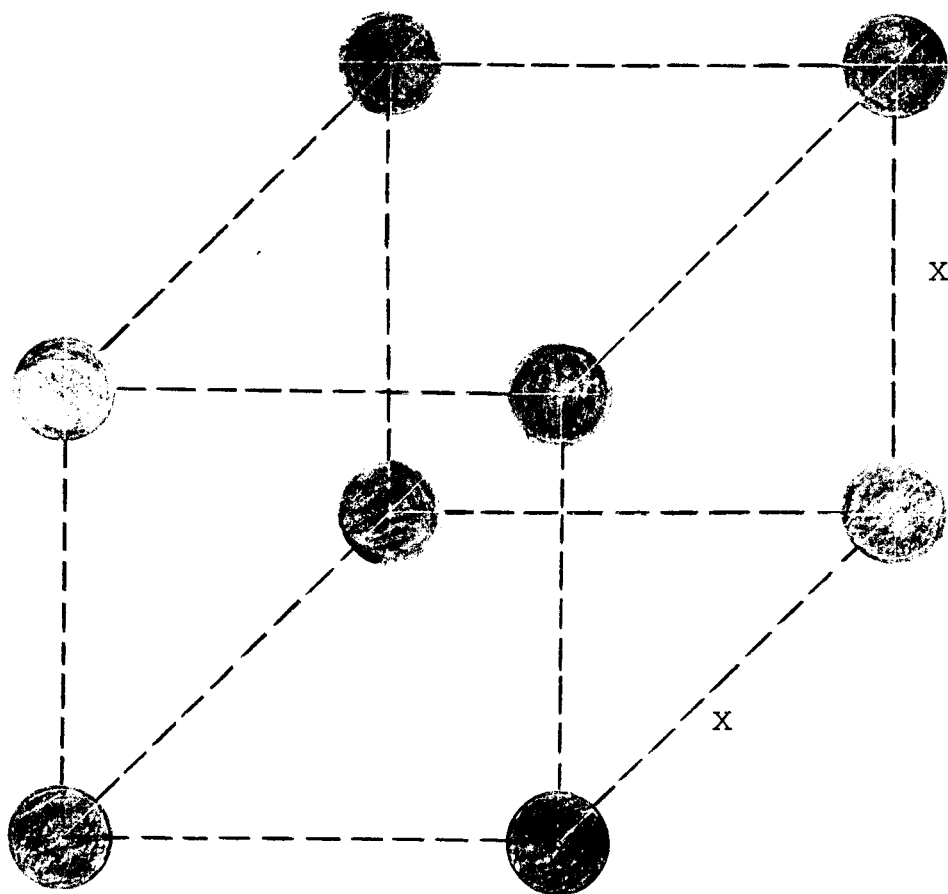
Figure 2

THE INTERPARTICLE DISTANCE IN A
MAXIMUM SEPARATION UNIFORM ARRAY

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A graph of the realtionship (Equation 3) is shown in Figure 3. The volume concentration at which the particles touch is that for y = 1. For nonspherical particles in random array the values read from the curve in Figure 3 will not be exact but the value obtained will indicate the order of magnitude for intersurface separation.

B. General Analysis of Multiple Interaction Phenomena

1. Solid Angles Subtended in Multiple Particle Systems

The discussion given here is limited to spherical particles. An important factor determining the effects of multiple scattering within a cloud of particles is the distance between the particles. Since the scattered light from a particle is non-homogeneous in space the interaction with a particle at a given distance will vary with its orientation in space with respect to the direction of the incident beam and the center of the prime scattering particle. A general relationship concerning the position of the second particle can be expressed as follows. For a plane wave incident on a spherical particle as shown in Figure 4, the second particle shown subtends a solid angle $\emptyset$ defined by

$$\emptyset = \frac{\text{Projected area of particle}}{R^2} = \frac{(\pi/4)d^2}{R^2}$$

If the x, y, z, coordinates of the system shown in Figure 4 are defined by the fact that the y, z, plane is perpendicular to the direction of the incident radiation, it follows that
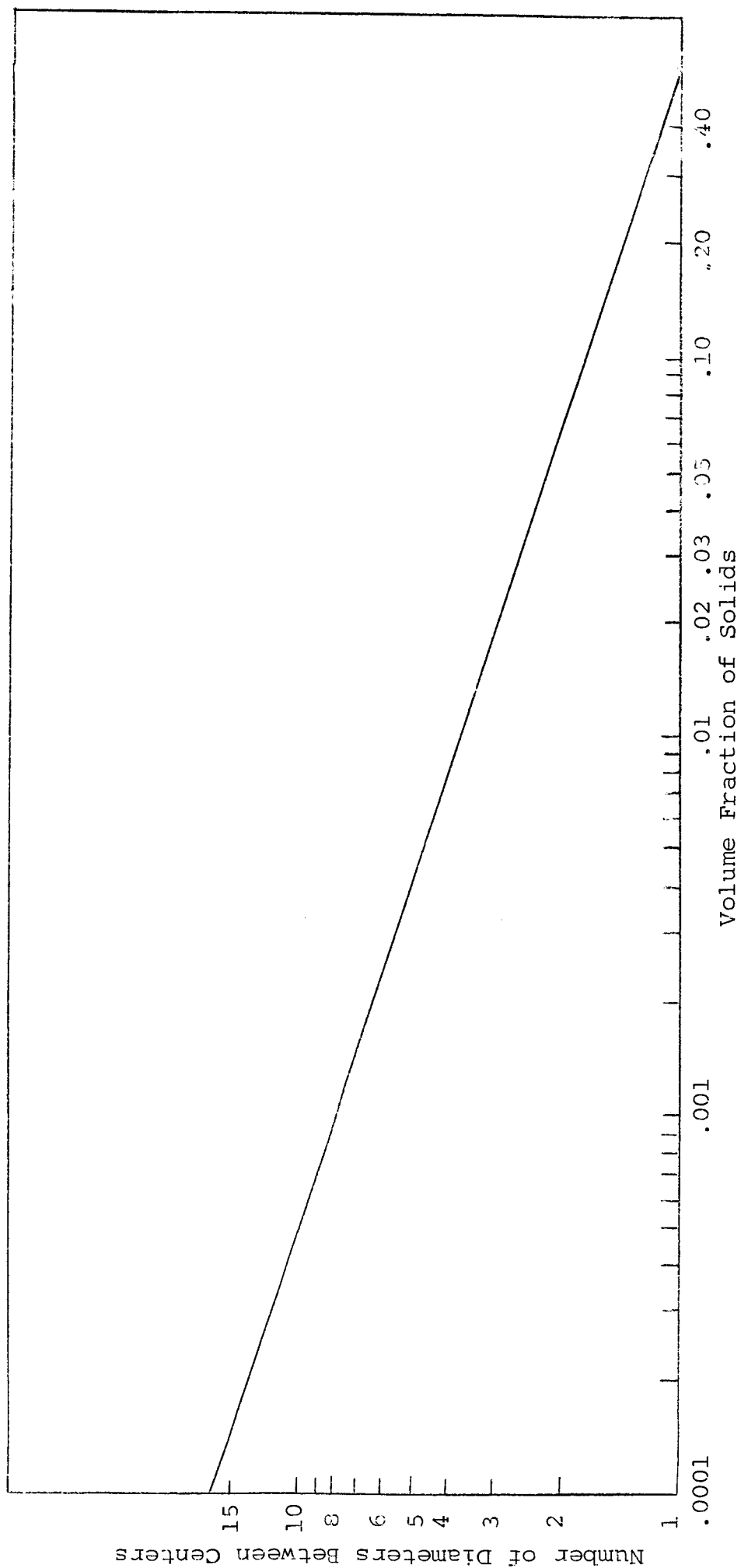
Figure 3

RELATIONSHIP BETWEEN VOLUME FRACTION OF SOLIDS AND INTERPARTICLE DISTANCE
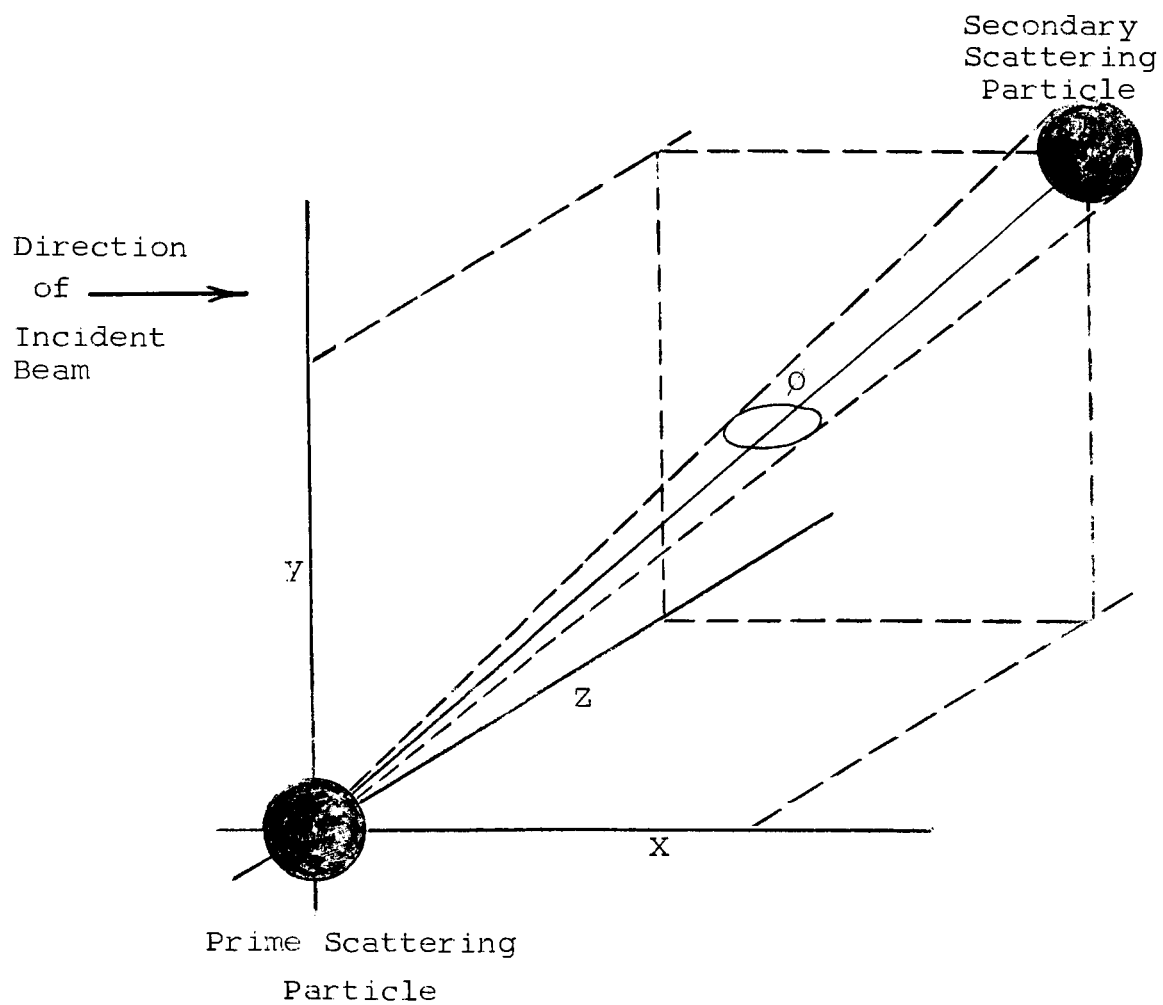IN A MONOSIZED MAXIMUM INTERPARTICLE DISTANCE ARRAY

Direction
of ⟶
Incident
Beam

Secondary
Scattering
Particle

Y

ρ

Z

X

Prime Scattering
Particle

Figure 4

RELATION OF PRIME TO SECONDARY
SCATTERING PARTICLES

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$$R^2 = x^2 + y^2 + z^2$$

and therefore

$$\emptyset = \frac{\pi}{4} \frac{d^2}{x^2 + y^2 + z^2}$$

Let the general function for the distribution of the scattered energy from the prime scattering particle be

$$F(\Phi)_{xyz}$$

where $F(\Phi)$ denotes a general function of Φ and x, y, z, are the coordinates of the line joining the center of the particle to the centroid of the area defining the solid angel Φ. Now the solid angle of influence of the second scattering particle will be greater than its nominal solid angle since radiation adjacent to the perimeter is also affected by the particle. Let σ be an extension parameter such that $\emptyset\sigma$ is the area over which the particle influences the incident radiation. At the present stage of development of the theory we assume that σ is a function of d/λ, the ratio of the particle diameter and S. the direction and λ the wavelength of the radiation considered.

A quantity which we believe important in predicting the effects of multiple interaction is the solid angle subtended by a particle which is a specific number of diameters away from secondary particles, i.e., R is expressed as a number of diameters.

Let $R = yd$

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The solid angle subtended $\emptyset = \dfrac{\pi d^2}{4} \div y^2 d^2$

$$\emptyset = \dfrac{\pi}{y^2 4}$$

Now the scattered energy is distributed into 4π radians. The numerical fraction of scattered energy intercepted by a particle y diameters from first particle is given by

$$(f)_y = \dfrac{\pi}{y^2 4} \div 4\pi$$

$$(f)y = \dfrac{1}{y^2 16} \tag{4}$$

A plot of this relationship (Equation 4) is given in Figure 5.

2. <u>The Probability Distribution of Interparticle Distances With a Dilute Cloud of Particles</u>

An approximation to the interparticle distance within a cloud of particles in which the particles are randomly distributed can be obtained in the following manner.

Consider a single reference sphere as shown in Figure 6. At the closest approach of a second sphere to the first sphere the center of the second sphere lies on a sphere of radius 2 r (illustrated in Figure 6). Let us consider a portion of the cloud defined by the radius S and let this be termed the sphere of study. Now let the sphere of study be divided into x spherical shells of thickness ρ. The volume of the mth spherical shell is $4\pi \left[2 r + m \, x\rho \right]^2$. Volume of sphere of study $= 4\pi \left[2 r t x \rho \right]^2$.
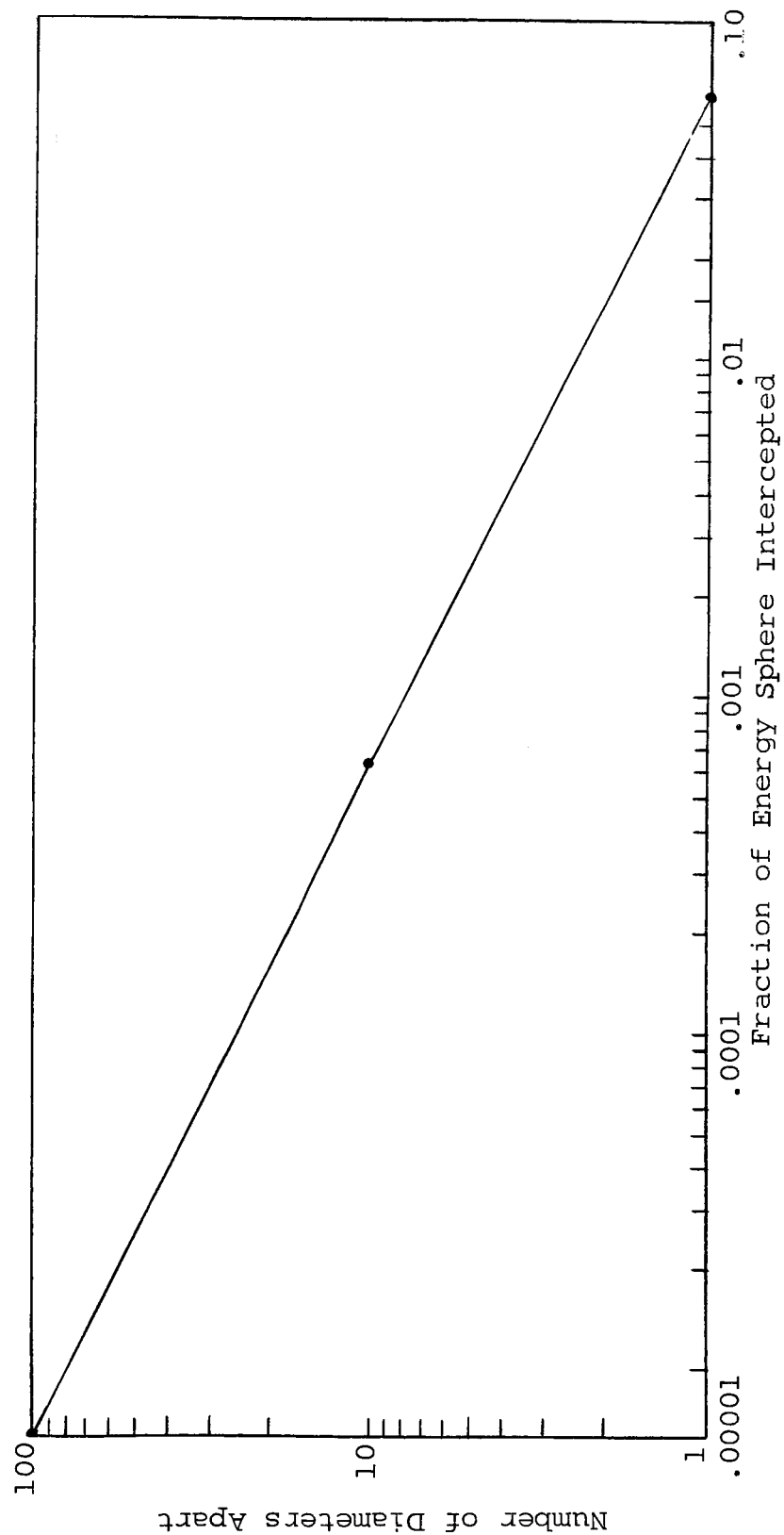
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Figure 5

FRACTION OF ENERGY SPHERE INTERCEPTED AT ANY GIVEN DIAMETER
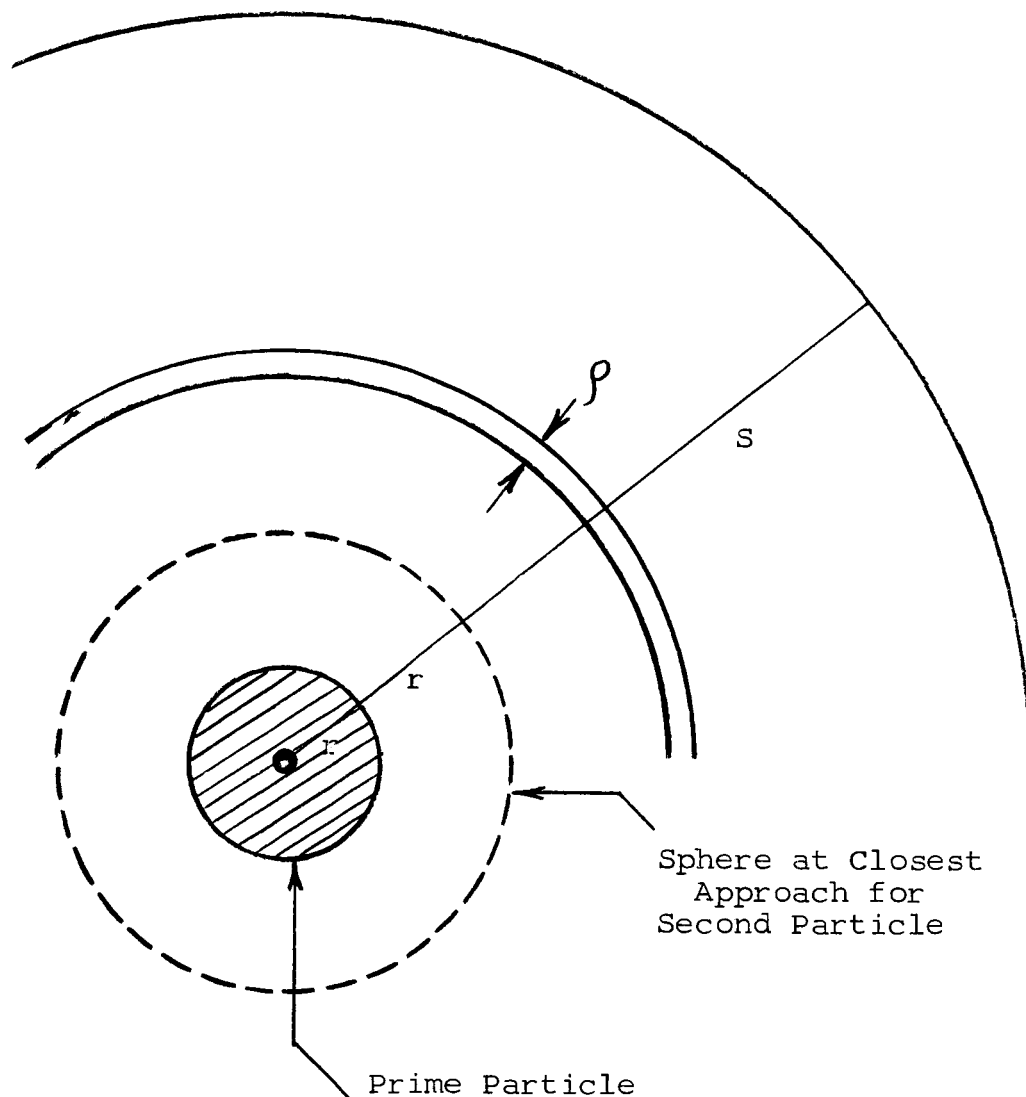SEPARATION OF TWO EQUAL SPHERES

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Figure 6

REFERENCE SPHERE FOR DETERMINING
PROBABILITY DISTRIBUTION OF
INTERPARTICLE DISTANCES WITHIN A DILUTE CLOUD

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∴ The probability that the second sphere center lies within the mth shell is given by

$$P_m = \sum_{i=o}^{i=x} \frac{4\pi \left[2r + m\rho\right]^2 \rho}{4\pi \left[2r + i\rho\right]^2 \rho} \qquad (5)$$

Now

$$\sum_{i=o}^{i=n} 4\pi \left[2r + i\rho\right]^2 \rho = \text{Volume of shell which can contain the particle center}$$

$$= \frac{4}{3} \pi \left[s^3 - d^3\right]$$

$$\therefore P_m = 3 \frac{\left[d + m\rho\right]^2 \rho}{s^3 - d^3} \qquad (6)$$

If we consider a certain volume of the cloud then on the average the number of particles in this portion of the cloud is given by the expression $(N)_V = V \cdot n = \dfrac{\alpha V}{V_p}$

where

      V = volume of cloud selected

      α = solids fraction of unit volume

      n = number of particles/unit volume

      V_p = volume of particle

If N is a very large number then to the first order of magnitude any sample of cloud of volume V isolated from the cloud would have N particles. As the absolute value of N decreased the actual number within the isolated portion would fluctuate at random.

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It is generally recognized that if N is approximately 25 then random fluctuations in the sampled volume are relatively small. Assuming then that N is greater than 25 and making the volume of the cloud studied the same as the study volume of the earlier derivation, we have

$$\frac{N}{\alpha} = \frac{V_s}{V_p}$$

Since $V_s/V_p = s^3/d^3$ then

$$\frac{N}{\alpha} = s^3/d^3 \tag{7}$$

Now let $\rho = \frac{d}{\beta}$ where β is some convienient number.

Then the number of shells of thickness ρ in the study volume is given by the expression

$$\gamma = \frac{S-d}{\rho} = \frac{(S-d)}{d}\beta$$

$$\gamma = \left[\left(\frac{N}{\alpha}\right)^{1/3} -1\right]\beta \tag{8}$$

Substituting for S, d and ρ in Equation 6 we obtain the equation

$$P_m = \frac{3}{\beta}\left[\frac{1 + m\beta}{\frac{N}{\alpha} -1}\right] \quad \text{for } m = 1 \rightarrow \gamma \tag{9}$$

It should be noted that by expressing all distances in fractions of a diameter, an expression which is independent of the particle diameter has been attained. (A check on the validity of the equation is provided by the fact that all re-lationships are dimensionally correct).

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Another general relationship which will be useful in discussing multiple interaction is the value of P_m in terms of P_1 the probability that the first shell is occupied. We note

$$\frac{P_m}{P_1} = \frac{3}{\beta} \left[\frac{1 + m\beta}{\frac{n}{\alpha} - 1} \right] \cdot \frac{\beta}{3} \left[\frac{\frac{N}{\alpha} - 1}{1 + \beta} \right]$$

$$\frac{P_m}{P_1} = \frac{1 + m\beta}{1 + \beta} \qquad\qquad (10)$$

With the aid of these general equations we can draw up a descriptive array in two dimensions of a three-dimensional cloud. In the following sections specific systems are studied with the help of these equations and the implications of the general results for studies of multiple scattering.

3. Application to Rain Clouds

We now use the general equations to discuss the probability of multiple interaction within any given system. Let us first consider the case of a rain cloud. Typical concentations of rain clouds are 200 particles/cm^3 of mean diameter 10 μ. Since we are interested in orders of magnitudes primarily, let us calculate the volume fraction of a rain cloud containing 200 particles each of 10μ diameter. Volume concentration of

$$\text{water/cc} = 2 \cdot 10^2 \cdot (10 \times 10^{-4})^3 \cdot \frac{\pi}{6}$$

$$= \frac{2\pi}{6} \times 10^{-7} \text{ cubic cm}$$

$$= 10^{-7} \text{ cubic cm}$$

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i.e., α [volume fraction of water] $= 10^{-7}$

From Equation 3

$$y = 0.806 \times \sqrt[3]{10^7}$$

$$= 0.806 \times 10 \sqrt[3]{10} \text{ diameters}$$

$$= 1.74 \times 10^2 \text{ diameters}$$

where y is the average interparticle distance as defined in section II.A.

Therefore we see that the average interparticle distance within a cloud is of the order of 170 diameters.

As already stated a sample of cloud containing approximately 25 drops is a convenient sample in which fluctuations due to random sample can be expected to be reasonably small. Therefore, to calculate the probabilities of a second particle being within any given number of diameters of a prime scattering particle, let us consider a study volume containing 25 cloud droplets. From Equation 8

$$\gamma = \left[\left(\frac{25}{10^{-7}} \right)^{1/3} -1 \right] \beta \qquad (11)$$

where γ = number of probabilities shells of width β.

Let us take $\beta = 1$ diameter.

Then the number of shells studied is

$$\gamma = \left[(0.25 \quad 10^9)^{1/3} - 1 \right]$$

$$= 629$$

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For the case where $\beta = 1$ Equation 10 becomes

$$P_m = P_1 \; \frac{1 + m}{2}$$

$$= \frac{P_1 (1 + m)}{2}$$

Choosing P_1, the probability that, the second center is in shell 1 as 2 units

$$P_m = 1 + m \text{ units}$$

$$\text{Total probability units} = \sum_{i = 0}^{i = 620} (1 + i)$$

$$= 620 + \frac{620^2}{2}$$

$$= 1.928 \times 10^5$$

In the next report this fact will be used to show that in rain clouds multiple scattering involving significant amounts of energy are very rare events. Further application of this relationship to other systems will be developed.

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